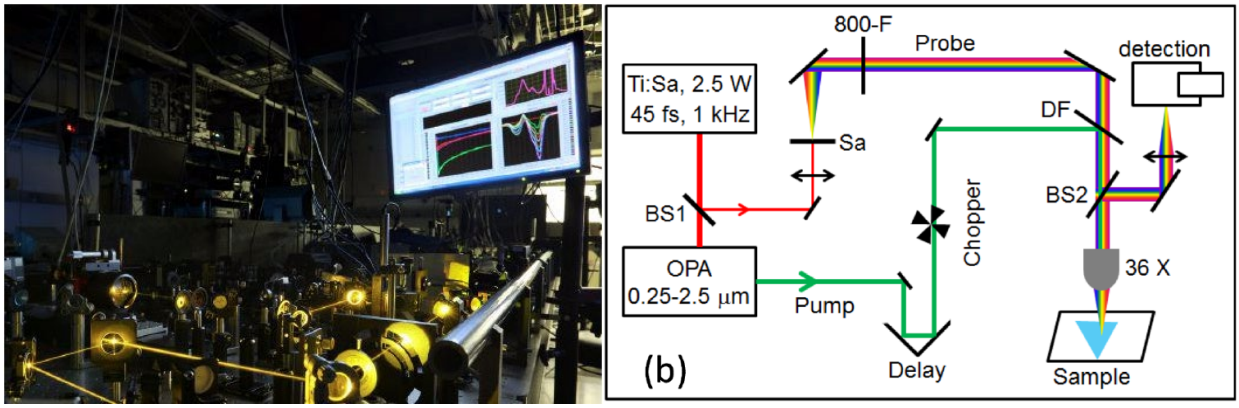
Femtosecond pump-probe spectroscopy



Scientists use a femtosecond pump-probe setup at CNMS to characterize ultrafast carrier dynamics in new emerging two-dimensional (2D) and other materials. This system allows one to study pathways and dynamics of electronic excitations that is crucial for accelerating the development of new artificially structured functional materials for electronic and optoelectronic applications.

Technical description:

Femtosecond pump-probe spectroscopy. A home-built femtosecond pump-probe spectrometer (PPS) was used to measure ultrafast exciton dynamics in 2D crystals and other materials. The PPS is based on a titanium sapphire (Ti:Sa) oscillator (Micra, Coherent) with its output seeding a Ti:Sa Coherent Legend (USP-HE) amplifier operating at 1kHz repetition rate. The Legend amplifier provides pulses centered at 800 nm, with 45 fs duration and 2.2 mJ energy per pulse. The output of the Legend amplifier was divided onto two portions: 90%was used to generate tunable excitation pulses in an optical parametric amplifier (TOPAS, Coherent), and the second one (10%) was used to generate the white-light continuum (WLC) probe in a 2-mm-thick sapphire window. The WLC which covers the spectral range from 450 to 900 nm was collimated and focused using parabolic mirrors to minimize temporal chirp. The transmitted WLC after the sample was sent for detection through a 100-μm-core optical fiber coupled with a spectrometer-linear CCD array (USB2000ES, Ocean Optics). The pump beam was sent through a controllable optical delay line and was chopped at 500 Hz frequency to allow absorption changes in the transmitted probe to be measured between every two successive laser shots. At the sample, the probe and pump spot sizes were ~50 and ~100μm, respectively.

For measurements of individual 2D crystals, the pump and probe beams are sent to the sample collinearly and focused down to sub-10-μm spot sizes with a 36x reflective objective. The reflected probe is detected by a spectrometer (Shamrock 303i, Andor) equipped with an electron multiplier (EM) CCD (Newton, Andor) (Figure b)

Applications

Ultrafast dynamics of metal plasmons induced by 2D semiconductor excitons in hybrid nanostructure arrays. Localized surface plasmon resonances are actively considered to improve the efficiency of metal based photocatalysis, photodetection, and photovoltaics. Here, we show an example on the exchange of energy and electric charges in a hybrid composed of a two-dimensional tungsten disulfide (2D-WS_2) monolayer and an array of aluminum (Al) nanodisks (**Figure 1**). Femtosecond pump-probe spectroscopy results indicate that within ~830 fs after photoexcitation of the 2D-WS_2 monolayer energy transfer from the 2D-WS_2 excitons excites the plasmons of the Al array. Then, upon the radiative and/or nonradiative damping of these excited plasmons, energy and/or electron transfer back to the 2D-WS_2 semiconductor

takes place as indicated by an increase in the reflected probe at the 2Dexciton transition energies at later time delays. This simultaneous exchange of energy and charges between the metal and the 2D-WS_2 semiconductor resulted in an extension of the average lifetime of the 2D-excitons from ~15 ps to ~58 ps in the absence and presence of the Al array, respectively. The indirectly excited plasmons were found to live as long as the 2D-WS_2 excitons exist. The demonstrated ability to generate exciton-plasmon coupling in a hybrid nanostructure may open new opportunities for optoelectronic applications such as plasmonic-based photodetection and photocatalysis.

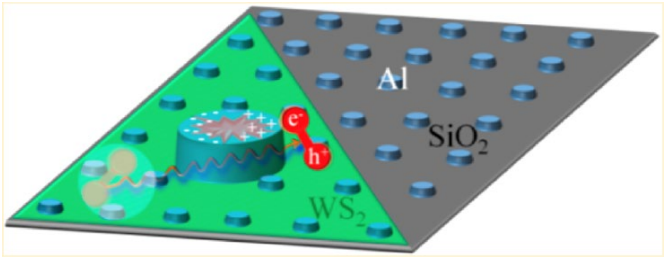


Figure 1. WS_2-monolayer and Al-nanodisk array system used for investigation of exciton pathways and dynamics. Boulesbaa et al, *ACS Photonics* **3**, 2389 (2016)

Ultrafast Charge Transfer and Hybrid Exciton Formation in 2D/0D Heterostructures. Photoinduced interfacial charge transfer is at the heart of many applications, including photovoltaics, photocatalysis, and photodetection. With the emergence of a new class of semiconductors, i.e., monolayer two-dimensional transition metal dichalcogenides (2D-TMDs), charge transfer at the 2D/2D heterojunctions has attracted several efforts due to the remarkable optical and electrical properties of 2D-TMDs. Unfortunately, in 2D/2D heterojunctions, for a given combination of two materials, the relative energy band alignment and the charge-transfer efficiency are locked. Due to their large variety and broad size tunability, semiconductor quantum dots (0D-QDs) interfaced with 2D-TMDs may become an attractive heterostructure for optoelectronic applications. Here, we show an example of femtosecond pump-probe spectroscopy to reveal the sub-45 fs charge transfer at a 2D/0D heterostructure composed of tungsten disulfide monolayers (2D-WS_2) and a single layer of cadmium selenide/zinc sulfide core/shell 0D-QDs (Figure 2). Furthermore, ultrafast dynamics and steady-state measurements suggested that, following electron transfer from the 2D to the 0D, hybrid excitons, wherein the electron resides in the 0D and the hole resides in the 2D-TMD monolayer, are formed with a binding energy on the order of ~140 meV, which is several times lower than that of tightly bound excitons in 2D-TMDs.

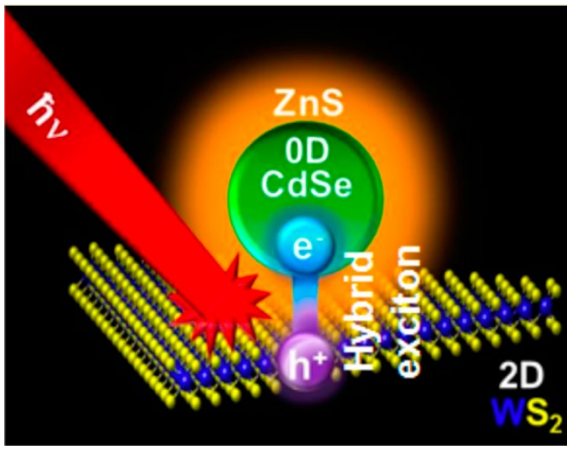


Figure 2. Schematic of a 2D/0D heterostructure for ultrafast charge transfer studies. Boulesbaa et al, *J. Am. Chem. Soc.* **138**, 14713 (2016)

Ultrafast Spectral Dynamics of Mixed-Halide Nanocrystals. In this work we investigated the spectral dynamics of cesium lead mixed-halide, $CsPb(Br_xCl_{1-x})_3$ perovskite nanocrystals probed with complementary spectral techniques: time-resolved photoluminescence and transient absorption spectroscopy (Figure 3). Mixed-halide perovskite nanocrystals were synthesized via a hot-injection method followed by anion exchange reactions. Our results show that increased Cl content in perovskite nanocrystals (a) diminished the photoluminescence quantum yield and gave rise to rapid radiative recombination of carriers; (b) resulted in rapid thermalization of hot carriers and low carrier temperatures, which suggests weaker hot-phonon bottleneck and Burstein-Moss effects; (c) decreased the bandgap renormalization energy, which suggests high exciton binding energy and poor charge extraction in Cl substituted perovskite nanocrystals; and (d) increased the number of carriers undergoing Auger losses, where Auger processes dominate over trap assisted recombination. These findings provide a generalized framework to guide

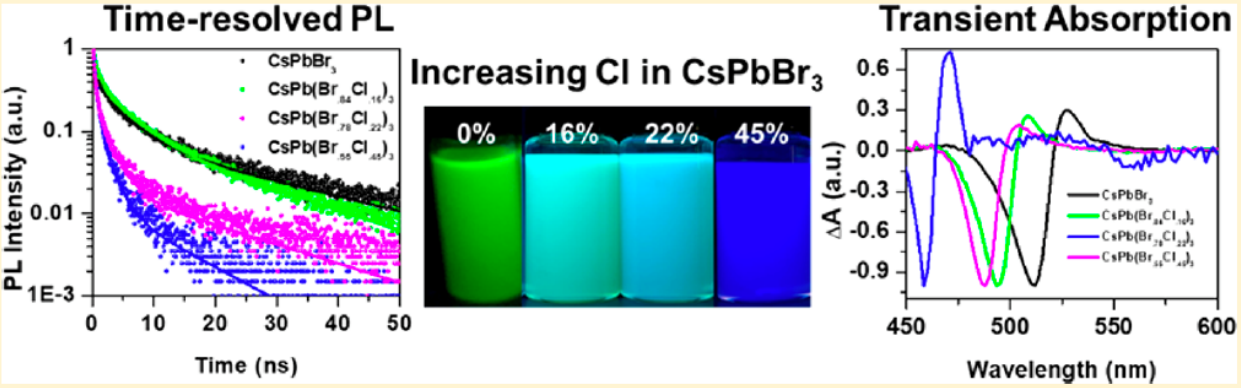


Figure 3. Time resolved photoluminescence and ultrafast transient absorption measured at different Cl concentrations in $CsPbBr_3$. Soetan et al, *ACS Photonics* **5**, 3575 (2018)

researchers as to when mixed-halide perovskite nanocrystals would be useful for optoelectronic technologies and when they would be detrimental to device performance.

Specifications:

Lasers for Raman excitation:

- Legend USP-HE (Coherent), 40 fs, 2.5 mJ/pulse, 800nm, 1kHz repetition rate.
- OPerA (TOPAS, Coherent) tunable from 0.3 to 2.6 μm.

Spectrometer:

- Shamrock 303i, Andor coupled with an EMCCD (Newton, Andor)

List of Highlights to be linked from the research highlights page

List of staff to be associated with the capability

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